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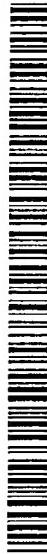
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(54) Title: WEATHERABLE COLORED RESIN COMPOSITIONS

(57) Abstract: Color stability of resinous compositions containing dyes which undergo chemical degradation upon exposure to ultraviolet radiation in the wavelength range of 300-400 nm is improved by incorporating therein an arylate polymer which is a 1,3-dihydroxybenzene isophthalate/terephthalate, preferably a resorcinol isophthalate/terephthalate. Other resins may also be present.

WEATHERABLE COLORED RESIN COMPOSITIONS

BACKGROUND OF THE INVENTION

This invention relates to coloration of synthetic resins, and more particularly to the provision of weatherable colored resins.

With the ever-expanding areas of use of synthetic resins and especially thermoplastic resins, it is of increasing interest to produce resinous compositions having many types of surface appearance, including coloration. Coloration of resins can be achieved by the use of dyes or pigments. One of the characteristics of pigments is their insolubility in the resin phase, which can lead to adverse consequences including loss of physical properties and loss of surface gloss. It is often preferred, therefore, to employ dyestuffs for coloration since they dissolve in the resin, forming a homogeneous composition which retains the gloss and advantageous physical properties characteristic of the neat resin.

A factor of concern in the coloration of synthetic resins is weatherability. Many dyes and other industrial colorants undergo photodegradation upon exposure to radiation of various wavelengths, often in the ultraviolet region of the spectrum. Thus, the resinous articles containing such colorants suffer a loss of color.

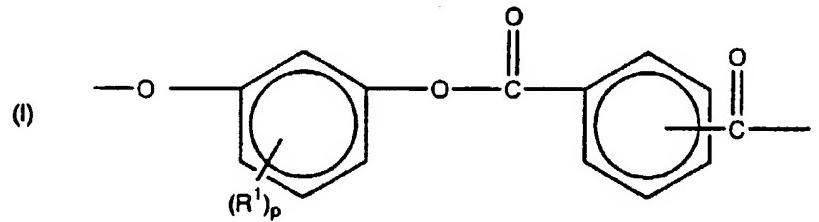
It is of increasing interest, therefore, to produce substantially color-stable resinous articles. It is of further interest to produce articles having a high degree of resistance to weathering and the color changes caused thereby.

SUMMARY OF THE INVENTION

The present invention is based on the discovery that certain arylate polymers absorb radiation in a region of the ultraviolet spectrum that can adversely affect the coloration of many dyes and other colorants for resins. In particular, such arylate polymers absorb in the 300-400 nm region. Thus, their presence protects the colorants from photodegradation and improves color stability.

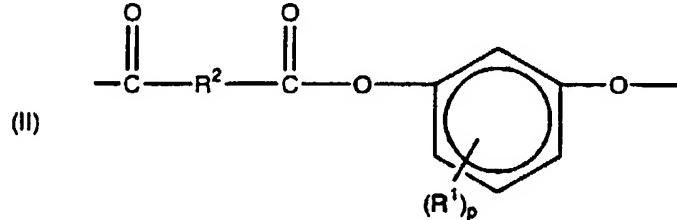
One aspect of the invention, therefore, is resinous compositions comprising the following and any reaction products thereof:

(A) an arylate polymer which is a 1,3-dihydroxybenzene isophthalate/terephthalate comprising structural units of the formula



5

optionally in combination with structural units of the formula



wherein each R¹ is a substituent, R² is a divalent C₃₋₂₀ aliphatic, alicyclic or mixed aliphatic-alicyclic radical and p is 0-3; and

10 (B) at least one dye which undergoes chemical degradation upon exposure to ultraviolet radiation in the wavelength range of 300-400 nm.

Another aspect of the invention is resinous compositions comprising components A and B as defined above, and (C) at least one resin different from component A, and any reaction products thereof.

DETAILED DESCRIPTION; PREFERRED EMBODIMENTS

15 For the sake of brevity, the constituents of the compositions of this invention are defined as "components" irrespective of whether a reaction between said

constituents occurs at any time. Thus, the compositions may include said components and any reaction products thereof.

Component A, the arylate polymer, is a 1,3-dihydroxybenzene isophthalate/terephthalate comprising structural units of formula I. It may also contain other acid groups, such as those derived from aliphatic dicarboxylic acids such as succinic acid, adipic acid or cyclohexane-1,4-dicarboxylic acid, or from other aromatic dicarboxylic acids such as 2,6-naphthalenedicarboxylic acid, preferably in amounts no greater than about 30 mole percent. Most often, however, the base polymer consists of units of formula I, optionally in combination with units of formula II.

The units of formula I contain a resorcinol or substituted resorcinol moiety in which any R¹ groups are halo or C₁₋₁₂ alkyl or a mixture thereof, and p has the value of 0-3. Preferably R¹ groups are C₁₋₄ primary or secondary alkyl groups, i.e., methyl, ethyl, propyl or butyl with methyl being more preferred. The most preferred moieties are resorcinol moieties, in which p is zero, although moieties in which p is 1 are also excellent with respect to the invention. Said resorcinol moieties are most often bound to isophthalate and/or terephthalate moieties.

Said 1,3-dihydroxybenzene moieties are bound to aromatic dicarboxylic acid moieties which may be monocyclic, e.g., isophthalate or terephthalate, or polycyclic, e.g., naphthalenedicarboxylate. Preferably, the aromatic dicarboxylic acid moieties are isophthalate and/or terephthalate. Either or both of said moieties may be present. For the most part, both are present in a molar ratio of isophthalate to terephthalate in the range of about 0.25-4.0:1, preferably about 0.4-2.5:1, more preferably about 0.67-1.5:1, and most preferably about 0.9-1.1:1.

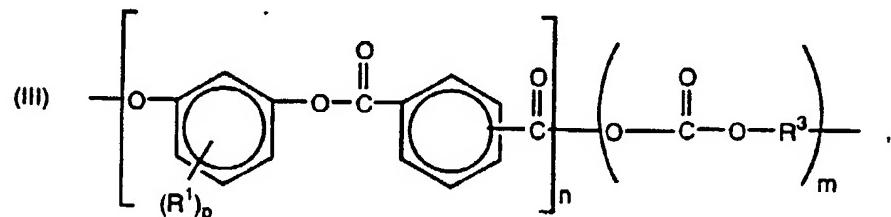
In the optional soft block units of formula II, resorcinol or substituted resorcinol moieties are again present in ester-forming combination with R² which is a divalent C₃₋₂₀ aliphatic, alicyclic or mixed aliphatic-alicyclic radical. Preferably, R² is a C₃₋₂₀ straight chain alkylene, C₃₋₁₂ branched alkylene, or C₄₋₁₂ cyclo- or

bicycloalkylene group. More preferably, R² is aliphatic and especially C₈₋₁₂ straight chain aliphatic.

It is usually found that the arylate polymers most easily prepared, especially by interfacial methods, consist of units of formula II and especially combinations of resorcinol isophthalate and terephthalate units in a molar ratio in the range of about 0.25-4.0:1, preferably about 0.4-2.5:1, more preferably about 0.67-1.5:1, and most preferably about 0.9-1.1:1. When that is the case, the presence of soft block units of formula II is usually unnecessary. If the ratio of units of formula II is outside this range, and especially when they are exclusively iso- or terephthalate, the presence of soft block units may be preferred to facilitate interfacial preparation. A particularly preferred arylate polymer containing soft block units is one consisting of resorcinol isophthalate and resorcinol sebacate units in a molar ratio between 8.5:1.5 and 9.5:0.5.

Arylate polymers useful as the base polymer may be prepared by conventional esterification reactions which may be conducted interfacially, in solution, in the melt or under solid state conditions, all of which are known in the art. Typical interfacial preparation conditions are described in copending application Serial No. 09/030,076, the disclosure of which is incorporated by reference herein.

Also useful as the base polymer are the block copolyestercarbonates disclosed and claimed in copending, commonly owned application Serial No. 09/181,902, the disclosure of which is also incorporated by reference herein. They include block copolymers comprising moieties of the formula



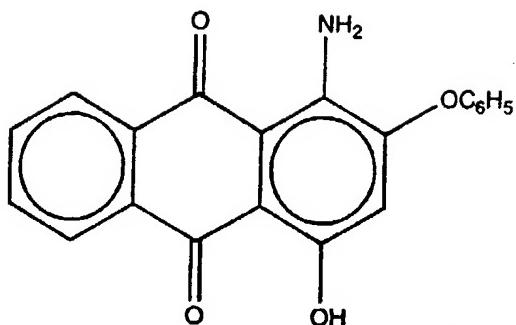
wherein R¹ and p are as previously defined, each R³ is independently a divalent organic radical, m is at least about 10 and n is at least about 4. Soft block moieties

corresponding to formula II may also be present. The most preferred moieties are again resorcinol moieties, in which p is zero.

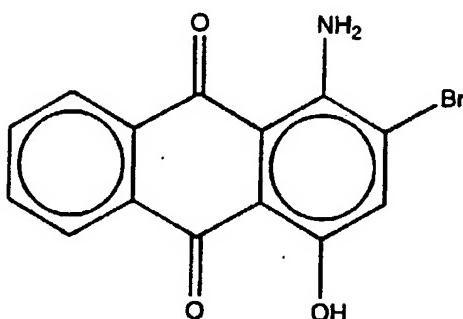
- In the organic carbonate blocks, each R³ is independently a divalent organic radical. Preferably, said radical comprises at least one dihydroxy-substituted aromatic hydrocarbon, and at least about 60 percent of the total number of R³ groups in the polymer are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. Suitable R³ radicals include m-phenylene, p-phenylene, 4,4'-biphenylene, 4,4'-bi(3,5-dimethyl)-phenylene, 2,2-bis(4-phenylene)propane, 6,6'-(3,3,3',3'-tetramethyl-1,1'-spirobi[1H-indan]) and similar radicals such as those which correspond to the dihydroxy-substituted aromatic hydrocarbons disclosed by name or formula (generic or specific) in U.S. Patent 4,217,438, which is incorporated herein by reference. A particularly preferred divalent organic radical is 2,2-bis(p-phenylene)isopropylidene and the dihydroxy-substituted aromatic hydrocarbon corresponding thereto is commonly known as bisphenol A.
- Such polyarylates may undergo a Fries rearrangement to form hydroxybenzophenone moieties. One of the properties of such moieties is their capability of absorbing ultraviolet radiation in the 300-400 nm region, and particularly in the 380-390 nm region. Thus, they have been found to provide protection against photodegradation for dyes which also absorb in this region.
- A number of such dyes are known in the art, and component B of the compositions of the invention comprises any of such dyes singly or in combination. They include phthalocyanine, anthraquinone, perinone, azo, quinophthalone and methine dyes. Illustrations are:

FILESTER BLUE GN: an (alkylamino)sulfonated copper phthalocyanine

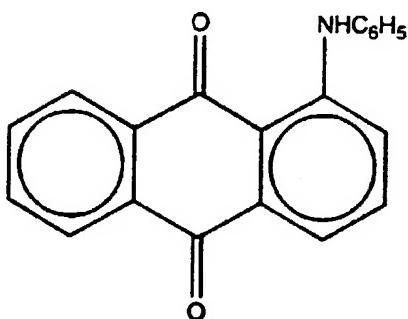
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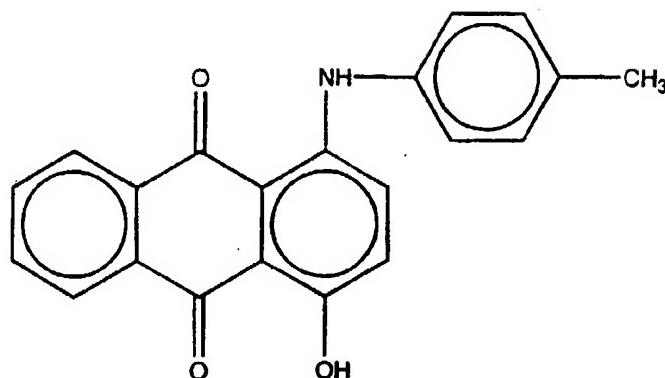
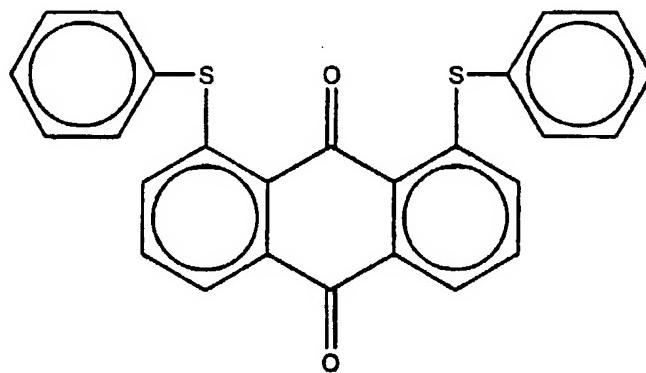
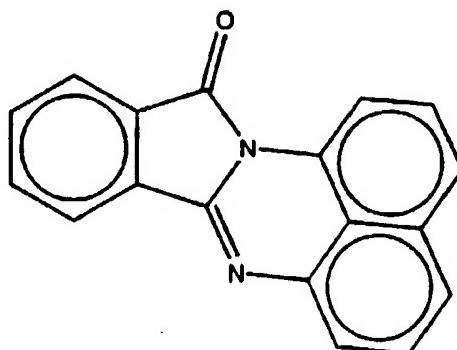


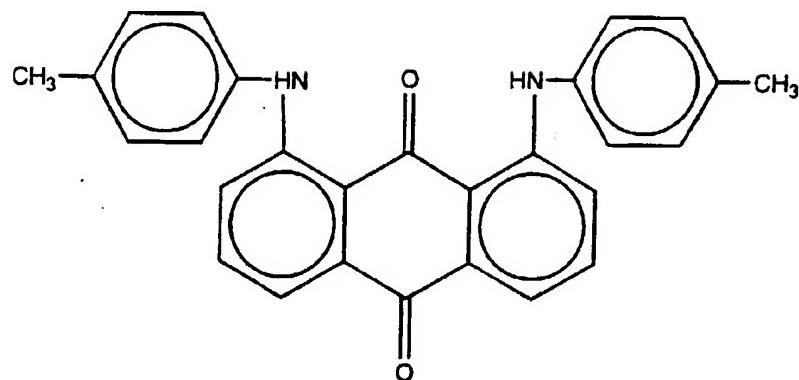
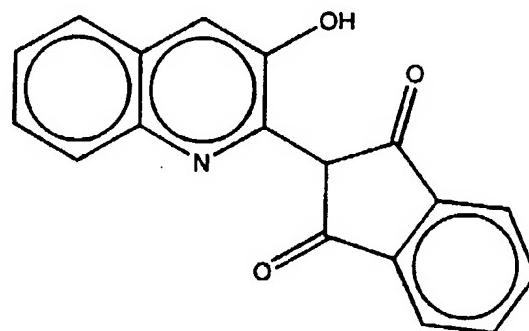
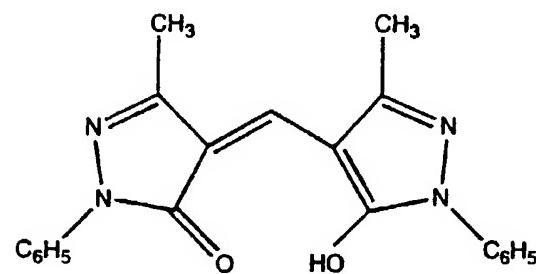
DIARESIN RED K:



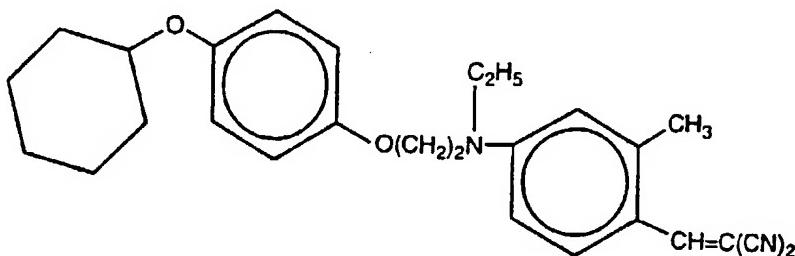
5 COLORPLAST RED LB:



MACROLEX VIOLET B:**AMAPLAST YELLOW GHS:**5 **AMAPLAST ORANGE LFP:****SOLVENT RED 195: a heterocyclic monoazo dye**

MACROLEX VIOLET 3R:**MACROLEX YELLOW G:**5 **MACROLEX YELLOW 3G:**

MACROLEX YELLOW 6G



It should be noted that other dyes are known to be sensitive to wavelengths in other regions of the spectrum, and their performance and stability may not be enhanced by combination with arylate polymers comprising component A. Examples of such dyes, the use of which is not considered part of the invention and the identities of which will be apparent to those skilled in the art or may be determined by simple experimentation, are various blue and green derivatives of 1,4-diaminoanthraquinone which are sensitive to wavelengths in the range of about 425-600 nm.

Resins suitable for use as component C are of virtually any molecular structure and include natural and synthetic, thermosetting or thermoset and thermoplastic resins. Blends of any of such resins may also be employed.

Natural resins include cellulosic resins and rubber. Of the synthetic resins, which are often preferred, thermoset and thermosetting resins include those derived from epoxy compounds, cyanate esters, unsaturated polyesters, diallyl phthalate, acrylics, alkyds, phenol-formaldehyde (including novolaks and resoles), melamine-formaldehyde, urea-formaldehyde, bismaleimides, PMR resins, benzocyclobutanes, hydroxymethylfurans and isocyanates.

Thermoplastic resins include addition and condensation polymers.

Condensation polymers are exemplified by polyesters, polyamides, polyethersulfones, polyetherketones, polyphenylene ethers, polyphenylene sulfides, polyimides and polyurethanes.

- 5 Illustrative addition polymers include homopolymers and copolymers of the following:

10 Esters of unsaturated alcohols, such as allyl and vinyl alcohols and butenediol, with saturated acids such as acetic, propionic, butyric, valeric, caproic and stearic; with unsaturated acids such as acrylic and methacrylic, with polybasic acids such as oxalic, succinic and adipic; with unsaturated polybasic acids such as maleic and fumaric; and with aromatic acids, e.g., benzoic, phthalic and terephthalic acids.

15 Esters of saturated alcohols, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, 2-ethylhexyl and cyclohexyl alcohols, ethylene glycol and diethylene glycol, with unsaturated aliphatic monobasic and polybasic acids, examples of which appear above.

Vinyl cyclic compounds, including styrene, methylstyrenes, divinylbenzene, vinylpyridines and N-vinylpyrrolidinone.

Unsaturated ethers such as methyl vinyl ether.

Unsaturated ketones, e.g., methyl vinyl ketone and ethyl vinyl ketone.

20 Unsaturated amides, e.g., acrylamide, methacrylamide, N-methylacrylamide, diacetone acrylamide and 2-acrylamido-2-methylpropanesulfonic acid and salts thereof.

Unsaturated aliphatic hydrocarbons, for instance, ethylene, propylene, isobutene, butadiene, isoprene, 2-chlorobutadiene and α -olefins in general.

25 Vinyl halides, e.g., vinyl fluoride, vinylidene fluoride, vinyl chloride and vinylidene chloride.

Unsaturated acids, examples of which appear above.

Unsaturated acid anhydrides, e.g., maleic anhydride.

Unsaturated nitriles, e.g., acrylonitrile and methacrylonitrile.

The preferred addition polymers include homopolymers and copolymers,
5 especially homopolymers of alkenylaromatic compounds, such as polystyrene,
including syndiotactic polystyrene, and copolymers of alkenylaromatic compounds
with ethylenically unsaturated nitriles, such as acrylonitrile and methacrylonitrile;
dienes, such as butadiene and isoprene; and/or acrylic monomers, such as ethyl
acrylate. These latter copolymers include the ABS (acrylonitrile-butadiene-styrene)
10 and ASA (acrylonitrile-styrene-alkyl acrylate) copolymers.

The preferred polymers for use under many conditions as component C are
polycarbonates (hereinafter sometimes designated "PC"), polyesters, polyetherimides,
polyphenylene ethers and addition polymers. Related blends are disclosed in
copending, commonly owned application Serial No. 09/152,877, the disclosure of
15 which is incorporated by reference herein.

The polycarbonates in the 3-component compositions are most preferably
bisphenol A homo- and copolycarbonates. Polyesters are illustrated by poly(alkylene
dicarboxylates), especially poly(ethylene terephthalate) (hereinafter sometimes
designated "PET"), poly(1,4-butylene terephthalate) (hereinafter sometimes
designated "PBT"), poly(trimethylene terephthalate), poly(ethylene naphthalate),
20 poly(butylene naphthalate), poly(cyclohexanedimethanol terephthalate),
poly(cyclohexanedimethanol-co-ethylene terephthalate) and
poly(1,4-cyclohexanedimethyl-1,4-cyclohexanedicarboxylate), and especially
poly(alkylene arenedioates), with PET and PBT being preferred.

25 Copolyestercarbonates may also be used. They comprise, in addition to the
organic carbonate units, ester units such as isophthalate and/or terephthalate. The
copolystercarbonates which find use in the instant invention and the methods for
their preparation are well known in the art as disclosed in, for example, US Patents

3,030,331, 3,169,121, 3,207,814, 4,194,038, 4,156,069, 4,238,596, 4,238,597,
4,487,896 and 4,506,065.

Suitable base polymer blends may comprise miscible, immiscible and
compatibilized blends including, but not limited to, PC/ABS, PC/ASA, PC/PBT,
5 PC/PET, PC/polyetherimide, polyester/polyetherimide, polyphenylene
ether/polystyrene, polyphenylene ether/polyamide and polyphenylene ether/polyester.

The 2-component and 3-component compositions of the invention may be
prepared by such conventional operations as solvent blending and melt blending. A
particularly preferred method for blend preparation is melt blending such as by
10 extrusion. The blends may additionally contain art-recognized additives including
impact modifiers, UV screeners, flame retardants, fillers, stabilizers, flow aids, ester
interchange inhibitors and mold release agents. It is intended that the blend
compositions include simple physical blends and any reaction products thereof, as
illustrated, for example, by polyester-polycarbonate transesterification products.

15 The amount of component B in the compositions of the invention is typically
an amount effective to impart coloration thereto. This is most often an amount in the
range of about 0.01-5.0% by weight based on total resin.

Resin proportions in the 3-component compositions are subject to wide
variation. In general, component A will be present in an amount effective to impart
20 color stability. Since the surface portion of a resinous article receives the predominant
amount of radiation, the presence of component A in the surface region is most
important. This may be achieved by preparing a simple blend of the resins or by
fabricating a multilayer article with component A, in combination with component B,
constituting the surface layer. Simple blends may, for example, contain about 5-60%
25 by weight of component A based on total resin.

The invention is illustrated by the following examples.

EXAMPLES 1-12

The arylate polymer employed was a block copolyestercarbonate containing 50 mole percent bisphenol A carbonate units and 50 mole percent resorcinol isophthalate/terephthalate units (50 mole percent isophthalate). Samples (2 grams) of 5 the resin were dissolved with 10 milligrams (mg) of dye in 8 milliliters (ml) of chloroform. Films were cast using a 10 mil doctor blade and the solvent was evaporated to provide resin films with a thickness of 26-32 microns. *5000 ppm*

The films were placed in slide holders and exposed in a Ci35A weatherometer (B/B filter, 0.77 watts per square meter [W/m^2]) to a total exposure in the range of 10 2,000-2,200 kiloJoules (kJ). The optical density ratios ("ODR") of the weathered to the corresponding unweathered samples were determined and compared with controls in which the polymer was a commercially available bisphenol A polycarbonate and the solvent was methylene chloride. The results are given in the following table.

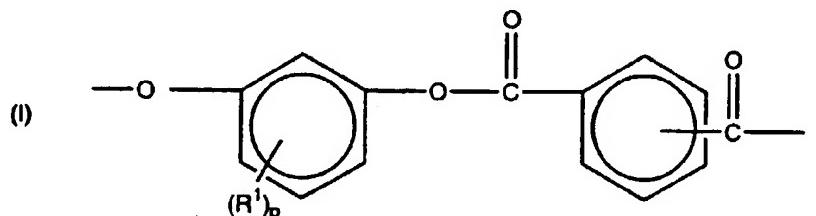
Example	Dye	ODR, example	ODR, control	% increase
1	FILESTER BLUE GN	0.710	0.287	248
2	FILESTER RED TBG	0.702	0.391	180
3	DIARESIN RED K	0.772	0.395	195
4	COLORPLAST RED LB	0.813	0.563	144
5	MACROLEX VIOLET B	0.759	0.519	146
6	AMAPLAST YELLOW GHS	0.811	0.677	120
7	AMAPLAST ORANGE LFP	0.665	0.469	142
8	THERMOPLAST RED 454	0.673	0.453	149
9	MACROLEX VIOLET 3R	0.716	0.452	158
10	MACROLEX YELLOW G	0.183	0.064	287
11	MACROLEX YELLOW 3G	0.771	0.377	205
12	MACROLEX YELLOW 6G	0.398	0.131	304

15 The effect of the arylate polymer on the color stability of the dye is apparent from the table.

WHAT IS CLAIMED IS:

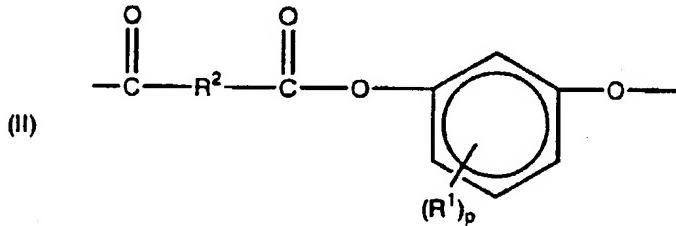
1. A resinous composition comprising the following and any reaction products thereof:

(A) an arylate polymer which is a 1,3-dihydroxybenzene isophthalate/terephthalate comprising structural units of the formula



5

optionally in combination with structural units of the formula



wherein each R¹ is a substituent, R² is a divalent C₃₋₂₀ aliphatic, alicyclic or mixed aliphatic-alicyclic radical and p is 0-3; and

10 (B) at least one dye which undergoes chemical degradation upon exposure to ultraviolet radiation in the wavelength range of 300-400 nm.

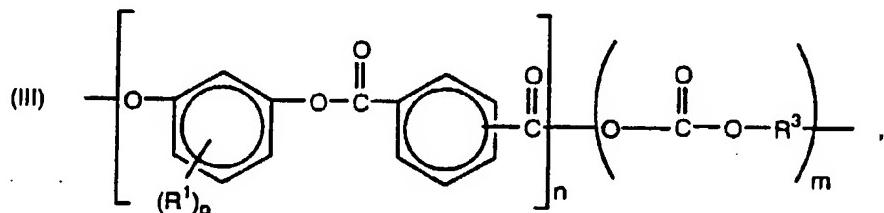
2. The composition according to claim 1 wherein component A consists of structural units of formula I and p is zero.

15 3. The composition according to claim 2 wherein the structural units are mixed isophthalate/terephthalate units.

4. The composition according to claim 1 wherein component A consists of structural units of formulas I and II, p is zero and R² is a C₈₋₁₂ straight chain aliphatic radical.

5. The composition according to claim 4 wherein the structural units of formula I are mixed isophthalate/terephthalate units.

6. The composition according to claim 1 wherein component A is a block copolyestercarbonate comprising structural units of the formula



10 each R¹ is a substituent, each R³ is independently a divalent organic radical, m is at least about 10, n is at least about 4 and p is 0-3.

7. The composition according to claim 6 wherein p is zero and R³ is 2,2-bis(p-phenylene)isopropylidene.

8. The composition according to claim 7 wherein the ester units are mixed isophthalate/terephthalate units.

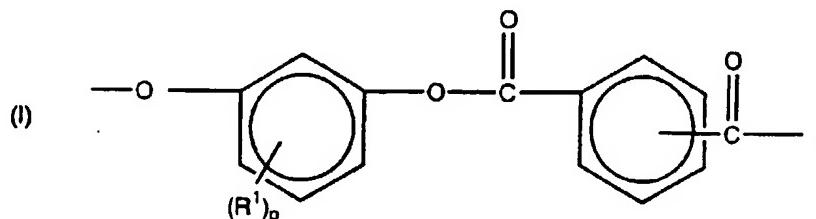
15 9. The composition according to claim 1 wherein the amount of component B is in the range of about 0.01-5.0% by weight based on total resin.

100 - 50,000 ppm

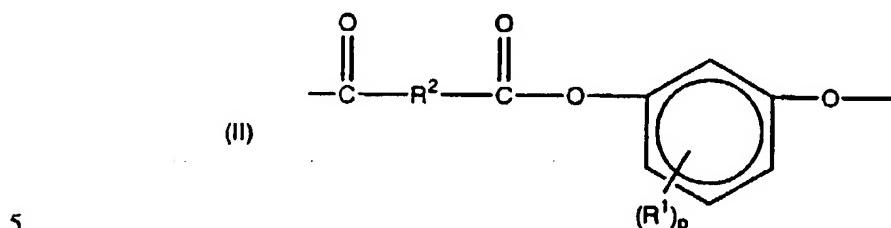
10. The composition according to claim 1 wherein component B is selected from the group consisting of phthalocyanine, anthraquinone, perinone, azo, quinophthalone and methine dyes.

20 11. A resinous composition comprising the following and any reaction products thereof:

(A) an arylate polymer which is a 1,3-dihydroxybenzene isophthalate/terephthalate comprising structural units of the formula



optionally in combination with structural units of the formula



5

wherein each R¹ is a substituent, R² is a divalent C₃₋₂₀ aliphatic, alicyclic or mixed aliphatic-alicyclic radical and p is 0-3;

10 (B) at least one dye which undergoes chemical degradation upon exposure to ultraviolet radiation in the wavelength range of 300-400 nm; and

(C) at least one resin different from component A.

12. The composition according to claim 11 wherein component C is a natural resin.

13. The composition according to claim 11 wherein component C is a synthetic resin.

15 14. The composition according to claim 13 wherein component C is a thermoset resin.

15. The composition according to claim 13 wherein component C is a thermoplastic resin.

16. The composition according to claim 15 wherein component C comprises at least one addition polymer.

17. The composition according to claim 16 wherein component C comprises an ABS or ASA resin.

5 18. The composition according to claim 15 wherein component C comprises at least one condensation polymer.

19. The composition according to claim 18 wherein the condensation polymer is at least one polymer selected from the group consisting of polycarbonates, polyesters, polyetherimides and polyphenylene ethers.

10 20. A resinous composition comprising the following and any reaction products thereof:

(A) a resorcinol isophthalate/terephthalate resin, and

15 (B) about 0.01-5.0% by weight, based on total resin, of at least one dye which undergoes chemical degradation upon exposure to ultraviolet radiation in the wavelength range of 300-400 nm, said dye being selected from the group consisting of phthalocyanine, anthraquinone, perinone, azo, quinophthalone and methine dyes.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/24235

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08L67/02 C08G63/181 C08G63/19 C08G63/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 083 115 A (UNION CARBIDE CORP) 6 July 1983 (1983-07-06) claims 1,5,6 ---	1-3,20
A	US 3 299 172 A (G.SCHADE ET AL.) 17 January 1967 (1967-01-17) claims 1,4,7; example 1 ---	1-3,6-8, 11,13, 15,18,19
A	US 3 792 118 A (KISHIKAWA H ET AL) 12 February 1974 (1974-02-12) column 3, line 3 - line 21; claim 1; examples 1,3 ---	1-3,13, 15-17
A	US 5 106 905 A (OKU SHOSUKE ET AL) 21 April 1992 (1992-04-21) column 3, line 1 - line 14; examples 1,2 ---	1,9-11, 20

Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
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